United States Patent [19]

Kowalski

[11] **3,928,147**

[45] **Dec. 23, 1975**

[54] **METHOD FOR ELECTROPLATING**

[75] Inventor: **Xavier Kowalski,** St. Louis, Mo.

[73] Assignee: **Monsanto Company,** St. Louis, Mo.

[22] Filed: **Oct. 9, 1973**

[21] Appl. No.: **404,562**

[52] **U.S. Cl.**..... **204/29;** 204/49; 204/52 R

[51] **Int. Cl.**[2].... **C25D 5/34;** C25D 3/12; C25D 3/38

[58] **Field of Search**..... 204/29, 49, 52 R; 148/6.15 R

[56] **References Cited**

UNITED STATES PATENTS

3,838,022 9/1974 Bartolini et al. ..... 204/32 R

Primary Examiner—John H. Mack
Assistant Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Wayne R. Eberhardt; Thomas B. Leslie

[57] **ABSTRACT**

Zinc die castings are treated with an aqueous solution of an organophosphorus chelating agent prior to immersion in the electroplating bath in order to inhibit immersion plating of Cu II from cyanide-free copper plating electrolytes.

11 Claims, No Drawings

METHOD FOR ELECTROPLATING

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the electrodeposition or electroplating of metals. More particularly, the present invention relates to a method for preventing or retarding immersion plating on cathodes having a strong electronegative potential by treating the cathode with an organophosphorus chelating agent prior to immersion in the metal plating electrolyte.

2. Description of Prior Art

Zinc die castings are widely used in the automotive industry. Most often the castings are provided with a decorative finish of chromium plate applied over a copper and nickel undercoat. The strong electronegative potential and high chemical activity of zinc creates special problems in the electroplating operation. Zinc reacts with both acid and alkali solutions and displaces the less active metals of copper and nickel from the electrolyte. Thus, in copper plating zinc castings, an acid electrolyte is not satisfactory because chemical deposition of copper takes place upon immersion of the zinc in the electrolyte and produces a copper film having poor adhesion and uniformity.

In modern electroplating operations, immersion plating of copper is avoided through the use of copper cyanide electrolytes. Although such systems are used extensively and give good plating results, cyanide electrolytes have certain characteristics which make their use generally undesirable. For example, the use of metal cyanide solutions can be hazardous since if the pH of the electrolyte should drop to neutral or below there is a danger of poisonous hydrogen cyanide gas being produced. Also, the use of metal cyanides presents a disposal problem due to their toxicity, and removing cyanides from waste solutions prior to disposal is an expensive operation.

It has recently been suggested to avoid the use of cyanide electrolytes by formulating electroplating baths with metal complexing agents. U.S. Pat. No. 3,475,293, for example, suggests the use of certain diphosphonates or monoamino lower alkylene phosphonates in electroplating divalent metal ions. U.S. Pat. Nos. 3,706,634 and 3,706,635 suggest combinations of ethylene diamine tetra(methylene phosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, and aminotri(methylene phosphonic acid) as particularly useful complexing compositions. U.S. Pat. No. 3,617,343 is similarly directed toward a nickel plating system employing certain phosphonic acid compounds.

Copper plating electrolytes based upon organophosphorus complexes rather than cyanide salts have a tendency to plate copper by immersion, resulting in a low quality plate. It is accordingly an object of the present invention to provide a method whereby immersion plating of copper in cyanide-free electrolytes may be avoided. It is a further object of this invention to provide a method for electroplating zinc and other active highly electronegative metals such as magnesium and aluminum with less electronegative metals such as copper, nickel, tin and alloys of such metals.

SUMMARY

In accordance with the present invention, zinc die castings which are to be copper plated from a copper organophosphorus complex electrolyte are pretreated with an aqueous solution of an organophosphorus chelating agent prior to immersion in the copper plating bath. The organophosphorus compound in the pretreating solution may be the same as or different than the organophosphorus compound in the copper plating electrolyte. Plating performance can be optimized by experimentation to select the best combination of organophosphorus compounds for any given system. Zinc alloys as well as magnesium and aluminum metals and alloys of these may be pretreated in a like manner prior to plating with copper, tin or nickel, or alloys thereof.

DESCRIPTION OF PREFERRED EMBODIMENTS

The electrodeposition of metals from cyanide-free electrolytes comprising aqueous solutions of a complex of the metal ion and an organophosphorus compound is well-known in the art as described, for example, in U.S. Pat. Nos. 3,475,293, 3,706,634 and 3,706,635. The teachings of these references with respect to metal plating from cyanide-free electrolytes are specifically incorporated herein by reference.

In cyanide-free electroplating processes wherein the cathode material is a metal having a stronger electronegative potential than the metal in solution, there is a tendency of the metal in solution to plate by chemical deposition as soon as the cathode material is immersed in the electrolyte. Electrolytic reduction potentials of representative metal ions at unit molar activity as reported in "Modern Electroplating" by Allen G. Gray, John Wiley and Sons (1953) are shown below. The potential for immersion plating exists where there is a significant difference in electrolytic potential between the metal being plated and the metal in solution.

ELECTROLYTIC POTENTIALS OF METALS IN VOLTS

Mg	−2.34	Sn	−0.136
Al	−1.67	Cu II	+0.345
Mn	−1.05	Cu I	+0.522
Zn	−0.762	Ag	+0.800
Cd	−0.402	Au	+1.42
Ni	−0.250		

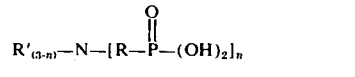
As is apparent from the above data, immersion plating problems are common when plating metals having an electronegative potential of greater than about −0.5, for example zinc, magnesium, or aluminum, with the more noble metals having electronegative potentials of less than about −0.5, such as cadmium, nickel, tin, copper, silver and gold. Of these combinations, plating of zinc die castings with copper is practiced on the greatest scale and the ensuing description of the instant invention will be directed to this specific embodiment of the invention with the understanding that the method of the present invention is equally applicable to other cathode metals and other plating metals as described above.

Chemical deposition or immersion plating of copper on a zinc cathode in a cyanide-free electrolyte is prevented or inhibited according to the method of this invention by treating the object to be plated with an aqueous solution containing an organophosphorus chelating agent prior to placing the cathode into the electroplating solution. While the treatment is most usually and conveniently accomplished by immersion, the zinc cathode may optionally be dipped, sprayed or otherwise exposed to the treating solution if preferred. Care should be taken to assure that all surfaces where im-

mersion plating is to be avoided are exposed to the pretreating solution.

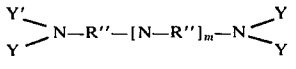
The organophosphorus compounds used in the pretreating solution may be any of a variety of compounds known to form metal ion complexes or ligands with zinc. For purposes of illustration, examples of such chelating agents are those organophosphorus compounds disclosed in U.S. Pat. Nos. 3,475,293 and 3,672,969, which disclosures are specifically incorporated herein by reference.

A preferred class of organophosphorus is the aminoalkylidene phosphonic acids conforming to the structure

I 

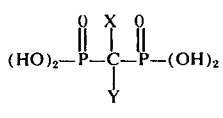
wherein R is a lower alkylidene radical preferably methylene, R' is hydrogen or an alkyl, hydroxy alkyl or carboxy alkyl radical having from 1 to about 12 carbon atoms, and *n* is an integer of from 1 to 3. Common examples of such compounds are aminotri(methylene phosphonic acid), methylaminodi(methylene phosphonic acid), carboxypentylaminodi(methylene phosphonic acid), and hydroxyethylaminodi(methylene phosphonic acid).

Another preferred class of organophosphorus compounds useful in the present invention are the polyaminoalkylene poly(alkylidene phosphonic acids) conforming to the structure

II 

wherein R'' is an alkylene of 2 to about 6 carbon atoms, *m* is from 0 to about 6, Y' is $CH_2P(O)(OH)_2$, and Y is Y' or $-CH_2CH_2OH$. Common examples of such compounds are ethylene diamine tetra(methylene phosphonic acid), bis(hexamethylene)triaminepenta(-methylene phosphonic acid, and bis(2-hydroxyethyl-)ethylene diamine di(methylene phosphonic acid).

Yet another preferred class of compounds are the lower alkylidene diphosphonic acids having the general structure

III 

wherein X is H, OH or NH_3 and Y is H or a C_{1-4} alkyl. Common examples of such compounds are methylene diphosphonic acid and 1-hydroxyethylidene-1,1-diphosphonic acid.

Yet other organophosphorus compounds capable of forming metal ion complexes with zinc and other cathode metals are known in the art and the use of such compounds in accordance with the teachings of the instant invention are within the scope of the invention.

The concentration of the organophosphorus chelating agent in the pretreating solution may be from about 0.1 to about 50% or higher up to the limit of solubility. For most chelating agents, low concentrations in the range of from about 0.5–2.0% are suitable for the practice of this invention.

In some applications, the pH of the pretreating solution may be adjusted to optimize results. In the case of zinc, lower pH values are preferred and good results are obtained at about pH 1.5 to 2.0. Optimum pH levels for any given system will depend upon the metal and organophosphorus chelating agent involved and optimum pH values may be easily determined by brief experimentation for each individual system.

The pretreatment operation may be conducted at room temperature or at elevated temperatures if preferred. The length of exposure of the metal being treated may be brief, often being no longer than the time it takes to immerse and remove the item being treated. In those cases where the organophosphorus compound is less active toward the metal, from 10 seconds up to about 1 minute of exposure may be desirable. Longer exposure times may, of course, be used if desired.

After pretreating in the organophosphorus solution, the object to be plated may be rinsed or transferred directly to the electroplating bath. Where the same organophosphorus compound is used in both the pretreating and plating baths, rinsing may be unnecessary. Where different organophosphorus compounds are used it may be desirable to rinse after the pretreatment to avoid contaminating the plating bath with the first organophosphorus compound. Rinsing may also be desirable where the same organophosphorus compound is used in both baths to maintain the concentration of organophosphorus compound in the electrolyte at the desired level.

The method of this invention is further defined and illustrated by the following examples which are provided for purposes of illustration only and are not limiting of the invention. In these examples, zinc cathodes were pretreated with various organophosphorus compounds prior to electroplating copper from a cyanide-free electrolyte. The effect of pretreating was determined first by observing the nature and extent of immersion plating occurring after 30 seconds immersion in the plating bath and second, by examining the quality of the final copper plate.

EXAMPLES

Preparation of plating solution

Plating solutions were prepared in deionized water by adding the selected organophosphorus compound, potassium hydroxide and cupric hydroxide in that order, then adding additional potassium hydroxide as required to adjust the pH. The concentrations of the organophosphorus compound and copper in the final electrolyte are specified in the tabulated data. The concentration of copper in these plating solutions was deliberately made higher than would normally be used in an electroplating operation in order to accentuate the immersion plating problem.

Electroplating test

The electroplating was conducted in a Hull cell which is standard equipment for evaluation of electroplating solutions as discussed in U.S. Pat. No. 2,149,344. Quality of plate was judged according to brightness, cover, adhesion and uniformity of appearance and color. Zinc cathodes 4 × 2¾ inches and copper anodes 2¾ × 2⅛ inches were used in the cell. Cathodes were prepared for plating by first cleaning in a warm detergent solution, rinsing in D.I. water, rinsing

in a 1% solution of HCl and finally rinsing again in cold D.I. water.

The zinc cathodes were immersed in the plating solution for 30 seconds without applying current to determine the extent of immersion plating. The degree of immersion plating ranged from heavy deposits which washed off easily with water to very light deposits which did not wash off. Electroplating was conducted at an applied current of one ampere for 2 minutes. Plating solutions were agitated during both immersion plating and electroplating tests.

EXAMPLE I

A series of plating tests were run using HEDP (1-hydroxyethylidene-1,1-diphosphonic acid) as the organophosphorus compound in both the pretreating and the plating solutions. The plating solution was maintained at pH 9.5. Other data on composition and pH of pretreating solutions were as shown in TABLE I. The effect of pretreating zinc castings with HEDP to reduce immersion plating of copper is clearly evident from these data. The data further show some advantage in maintaining a low pH in the pretreating bath. Minimum immersion plating was obtained in Run 4 where only a very light, tightly adhering deposit of metallic copper was deposited on the zinc cathode during the immersion period.

TABLE I

Run No.	Pretreating Solution % HEDP	pH	Plating Solution % HEDP	% Cu	Plating Results Immersion Plate	Electroplate
1	—	—	12	1.5	Heavy, loose	Poor
2	—	—	6	0.75	Heavy, loose	Poor
3	1.2	1.7	12	1.5	Light	Good
4	1.2	1.7	6	0.75	Very light	Fair to Good
5	0.6	1.7	12	1.5	Medium – Light	Good
6	1.2	9.5	6	0.75	Medium	Fair

EXAMPLE II

A series of electroplating tests were run using different pretreating compositions in combination with an electroplating solution comprising 10% HEDP, 5% EDTMP, 3.3% H_3PO_3, 1.3% potassium acetate and 1.5% copper at a pH of 9.5. The results of the test are presented in TABLE II.

TABLE II

Run No.	Pretreating Solution Additive	AVe. %	pH	Plating Results Immersion Plate	Electroplate
7	MDP	1.0	1.7	Very Light	Good
8	EDTMP	2.3	1.5	Very Light	Good

MDP - methylene diphosphonic acid
EDTMP - ethylene diamine tetra(methylene phosphonic acid)

The above examples are provided to illustrate the present invention as it may be practiced with commonly available organophosphorus chelating agents in the plating of zinc die castings with copper. Other chelating agents and other metal cathodes and electrolyte compositions can be used as discussed above.

The mechanism whereby treating active cathode materials with a chelating agent prior to electroplating serves to prevent or inhibit chemical deposition of the metal to be plated is not fully understood. While not wishing to be bound by theory, it is believed that the exposure to the pretreating solution causes the formation of a metal ligand film on the surface of the cathode, and that this film resists chemical displacement of the cathode metal either by decreasing its solubility or by changing its electronegative potential to more closely equal that of the metal ions in the electrolyte.

In the commercial application of the instant invention, a strike bath may be utilized between the pretreating solution and the electroplating bath. Strike baths are widely used in electroplating operations and are common in cyanide plating of copper. The strike bath is characterized by having a low concentration of metal in solution to minimize a tendency for chemical deposition of the metal being plated. Ideally, a thin coating of metal is deposited electrically from the strike bath and the work is then transferred to the electroplating bath where a heavier metal coating is deposited from a more concentrated solution.

In the case of the present invention where it is desired to electroplate in a cyanide-free system, the strike bath would also be cyanide-free and formulated around an organophosphorus compound as defined herein. The organophosphorus compound used in the strike bath may be the same as or different than the organophosphorus compounds used in the pretreating solution and in the electroplating bath.

As an illustration, the strike bath may contain from about 0.3 to about 1.5 percent dissolved copper and from about 5 to 20 percent of an organophosphorus compound such as 1-hydroxyethylidene-1,1-diphosphonic acid. The electroplating bath used in conjunction with such a strike bath may contain from about 1.0 to 3.0 percent dissolved copper and from about 5 to 20 percent 1-hydroxyethylidene-1,1-diphosphonic acid. The strike bath may, like the electroplating bath, contain in addition to the copper and the organophosphorus compound a variety of additives such as buffers, pH adjusters, conductivity agents, brighteners, and others which serve to enhance the performance of the bath. These and other variations in the instant invention will be apparent to those skilled in the art.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. In the method of electroplating die castings composed of zinc or zinc alloyed with at least one of magnesium and aluminum with a less electronegative metal or alloy in a cyanide-free electrolyte comprising an aqueous solution of a complex of said less electronegative metal or alloy and an organophosphorus compound,

the improvement which comprises contacting the cathode with an aqueous solution consisting essentially of from about 0.1 percent up to the limit of solubility of an organophosphorus chelating agent for said cathode prior to immersing the cathode in said electrolyte.

2. A method of claim **1** wherein the less electronegative metal is copper, nickel, tin, silver or gold.

3. A method of claim **1** wherein the organophosphorus compound of said electrolyte and said chelating agent are the same organophosphorus compound.

4. A method of claim **1** wherein said organophosphorus compound and said chelating agent are selected from the group consisting of amino C_{1-12} alkylidene phosphonic acid, polyamino C_{2-6} alkylene poly(C_{1-12} alkylidene phosphonic acid) and C_{1-5} alkylidene diphosphonic acid.

5. A method of claim **1** wherein said organophosphorus compound and said chelating agent are selected from the group consisting of 1-hydroxyalkylidene-1,1-diphosphonic acid and ethylene diamine tetra(methylene phosphonic acid).

6. In a method of electroplating die castings of zinc and alloys of zinc containing at least one of magnesium and aluminum with a more noble metal selected from the group consisting of copper and nickel in an electrolyte comprising an aqueous solution of said copper or nickel and an organophosphorus compound, the improvement which comprises contacting the zinc or zinc alloy prior to immersion in the electrolyte with an aqueous solution consisting essentially of from about 0.1 percent up to the limit of solubility of an organophosphorus chelating agent which is capable of forming a zinc ligand.

7. A method of claim **6** wherein said organophosphorus compound and said chelating agent are selected from the group consisting of amino C_{1-12} alkylidene phosphonic acid, polyamino C_{2-6} alkylene poly(C_{1-12} alkylidene phosphonic acid) and C_{1-5} alkylidene phosphonic acid.

8. A method of claim **6** wherein said organophosphorus compound and said chelating agent are selected from the group consisting of 1-hydroxyalkylidene-1,1-diphosphonic acid and ethylene diamine tetra(methylene phosphonic acid).

9. A method of claim **6** wherein the pH of said aqueous solution of said organophosphorus chelating agent is about 1.5 to 2.0.

10. A method of claim **6** wherein the concentration of said organophosphorus chelating agent in said aqueous solution is from about 0.5 to 2.0 percent.

11. A method of claim **6** wherein the organophosphorus compound of said electrolyte and said chelating agent are the same organophosphorus compound.

* * * * *